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13. ABSTRACT *(Maximum 200 words)* From a detailed analysis of the behavior of two general types of organic solvents for conducting polyaniline, we conclude that fully protonated polyaniline (ratio H+/PhN=0.5) can be dissolved in a given organic solvent only in cases where the PANI-(acid)0.5 complex is solvated by an appropriate solvating agent. At least 0.5 moles per PANI unit (PhN) of the solvating agent must be present (this amount is dependent on nature of counterion and solvent, for example for very polar counterion in non-polar solvent this value is 1.0). The solvating agent can be the solvent itself if it has strong hydrogen bonding moieties, an excess amount of protonic acid, or some neutral compound with strong hydrogen bounding moieties which is compatible with the solvent. We have shown clearly that the solution properties (solubility, conformation, etc.) of conducting PANI prepared by counterion induced processibility are strongly dependent on the interactions between the polymer chain, the counterions, and the co-solvent. The solid state properties (conductivity, crystallinity, etc.) of a PANI film processed from such a solution are dependent on the choice of counterion, solvent, and co-solvent. The co-solvent can be removed after processing without altering the solid state properties of the resulting polyaniline films or fibers. All experimental results

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INDUSTRIAL PRODUCTS BASED UPON PROCESSIBLE CONDUCTIVE POLYANILINE

FINAL TECHNICAL REPORT

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INDUSTRIAL PRODUCTS BASED UPON
PROCESSIBLE CONDUCTIVE POLYANILINE

Final Report : April 1995

UNIAX has been conducted research under an eighteen month Phase II SBIR grant sponsored by the Ballistic Missile Defense Organization and awarded by the Air Force Office of Scientific Research through contract N° F49620-93-C-0011. The goal of this Phase II research was to exploit the UNIAX discovery of surfactant counter-ion induced processibility of the conducting polymer polyaniline to develop commercially acceptable solvents and cross-linkable liquid systems for use in products including:

- conductive coatings;

- conductive paints;

- conductive epoxies.

The effective date of this contract was 15 February, 1993. The following report summarizes the progress made in the course of the sponsored research, and briefly notes the activities which have been taken to commercialize the resulting technology.

§1. Development of Environmentally Acceptable PANI-Complex/Solvent Systems.

Although polyaniline (PANI) has been investigated extensively since the beginning of this century, it is only in the past decade that this polymer has attracted interest as a conducting material. Its wide range of intriguing electrical, electrochemical and optical properties, coupled with its excellent environmental stability, make PANI attractive for use as an electronic material in a variety of applications.

In the past, PANI has often been categorized as an intractable polymer, particularly when it has been prepared as a conductive salt. In 1990, a team at UNIAX reported that high molecular weight polyaniline can be protonated to its conducting form and simultaneously dissolved in many common nonpolar or weakly polar organic solvents when use is made of functionalized protonic acids. These functionalized protonic acids are generically denoted $H^+(M^-\!\!-\!\!R)$, in which the counterion species, $(M^-\!\!-\!\!R)$, contains a functional group R that is chosen to be compatible with nonpolar or moderately polar organic liquids. In this initial work it was reported that the solubility of the polyaniline salts and the conductivity of solution-cast films strongly depend on the choice of both the counterion and the solvents. In some cases conducting polyaniline can be dissolved in certain organic solvents only in the presence of co-solvents. Furthermore, the

processibility and properties of the resulting conducting polyaniline are found to be strongly effected by the nature of counterions *and* the solvent or co-solvents. In this report we present the results of a detailed study of this complex dependence.

§2. Experimental

§2.1 General procedure for dissolution of electrically conductive polyaniline

Polyaniline emeraldine base (Neste Oy, h_{in}=1.2-1.3 dL/g at room temperature in 0.1 % w/w solution in H_2SO_4) was mixed while stirring in anhydrous ethanol with various protonic acids in the molar ratio of 0.5 per PANI repeat unit (denoted PhN). The temperature was raised to 50 °C for 30 minutes, and the ethanol was subsequently evaporated at room temperature. The nearly dried, dark powder of polyaniline salt was further dried in a vacuum oven at room temperature for 48 hours and then at 50 °C for an additional 24 hours.

For the first class of organic solvents which were identified (as defined below), PANI salts were added to the solvent in a container under nitrogen gas flow while vigorously stirring. For the second class of solvents, PANI complexes were mechanically mixed with the co-solvent and dried under vacuum for 24 hours at 50 °C, in order to eliminate water that might have been absorbed during sample preparation. Organic solvents that were dried over molecular sieve were added into the solid mixture in a closed container. For both classes of solvents, the closed containers were rotated for 2 hours at room temperature and subsequently placed in a sonicator at a bath temperature of 45-50 °C for 24-48 hours. The mixtures were then cooled to room temperature and centrifuged at 15,000 rpm to eliminate a small amount of insoluble matter. The PANI-salt concentrations of the resulting solutions were determined by evaporation of the solvent. The corresponding emeraldine base content was later determined by deprotonation of cast films through exposure to an 3% aqueous NH_4OH solution.

§2.2. Characterization of films cast from PANI solutions

The electrical conductivity of cast films were measured by the standard four-probe method.

§3. Results and Discussions

Organic species that dissolve PANI *in its conductive form* generally can be divided into two classes. The first class, hereafter designated Type I solvents, comprises substances with strong hydrogen-bonding groups, such as cresols, phenols, trifluoroethanol, dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP), formic acid and other strong acids. At room temperature, these substances are capable of readily dissolving conducting polyaniline salts that are fully protonated (molar ratio H^+/PhN = 0.5, where PhN refers to the polyaniline phenyl-N chain repeat unit with a

functionalized protonic acid of an appropriately chosen organic tail. For example, PANI-camphorsulfonic acid (PANI-CSA$_{0.5}$), can be easily dissolved in m-cresol to concentrations in excess of 10 % w/w.

A second class of organic solvent (designated Type II) are those species without hydrogen-bonding forming groups or those that have only very weak hydrogen bonding capability. Examples include toluene, xylene, decalin, chlorobenzenes, *etc.* Fully-protonated polyaniline salts can be dissolved in these solvents *only* in the presence of:

  i) an excess of the same or a different functionalized protonic acid (*i.e.* at a molar ratio of counterions/PhN > 0.5); or

  ii) particular co-solvents, the nature of which is discussed below.

We emphasize that polyaniline salts with H$^+$/PhN = 0.5 are completely insoluble in this second class of solvents, except in the case of relatively low molecular weight polyaniline oligomers. The excess material used in methods *i)* or *ii)* can be removed after processing without significantly affecting the conductivity of the resulting product.

There are some solvents that display a behavior that is in between that of these two "limiting" classes. For example, PANI-CSA$_{0.5}$ and PANI-DBSA$_{0.5}$ salts are slightly soluble at room temperature in chloroform and benzylalcohol (~1%). To increase this solubility, the H$^+$/PhN molar ratio must be increased (*i.e.* more protonated PANI must be used). However, since the optimally conducting PANI salt whose molar ratio is H$^+$/PhN = 0.5 can be dissolved in these solvents (although only at very low concentrations), we classify these liquids as solvents of the first type.

We have organized our experimental results on the behavior of PANI salts in organic liquids, and the corresponding solid-state properties derived materials processed in these solvents, according to the oversimplified separation in the above two major classes of solvents, *i.e.* Type I and Type II.

§3.1 Type I organic solvents for conducting PANI salts
§3.1.1 PANI-CSA$_{0.5}$

As indicated above, conducting PANI salts can be dissolved in Type I organic solvents without additives or excess protonic acid. We observed that both the solubility of the salts in these solvents and the conductivity of cast PANI films obtained from such solutions are strongly dependent on the chemical nature of the counterions *and* of the solvent. In this first section we

focus on the latter issue. Table 1 lists some organic solvents in which the PANI-CSA$_{0.5}$ complex can be readily dissolved.

Table 1.
Solubility of PANI-CSA$_{0.5}$ in some Type I organic solvents; and the conductivity of films cast from the corresponding solutions.

| Solvent	Solubility* (%w/w)	Conductivity** (S/cm)
m-cresol	2-10	200-400
o-cresol	2-10	224
p-cresol	2-10	200
trifluoro-*m*-cresol	2.5	149
a,a,a-trifluoro-*m*-cresol	2-4	42
2-ethylphenol	2	228
3-ethylphenol	3	221
4-ethylphenol	3	217
o-chlorophenol	4.2	157
m-chlorophenol	3.0	87
3-methoxyphenol	1	8
allylphenol	1-2	3
hexafluoropropanol	2-4	60
trifluoroethanol	2-6	57
hexafluoro-2-phenyl-2-propanol	2.1	13
octafluoropentanol	2.6	4
chloroform [CHCl$_3$]	0.5-2 ***	1
formic acid	2-4	10^{-2}
dimethylsufoxide [DMSO]	2-5	10^{-2}
tetramethylenesulfoxide	1-2	3×10^{-4}
N-methylpyrrolidone [NMP]	2-4	10^{-4}
benzylalcohol	0.5-2 ***	10^{-4}

*   at room temperature.
**   for reference, the conductivity of pressed films of PANI-CSA$_{0.5}$ powder is ~10 S/cm.
*** The solubility is increasing with CSA/PhN molar ratio exceeding 0.5.

The conductivity data of films cast from the corresponding solutions are also shown. From the data collected in this table, we draw the following conclusions:

1) The solvents listed are quite different in chemical nature. They include species that are lightly acidic (*e.g.* the as cresols), or strongly basic (*e.g.* NMP), or close to neutral (*e.g.* benzylalcohol or chloroform). However, all solvents that dissolve PANI-CSA$_{0.5}$ are organic substances capable of forming strong hydrogen bonds which enable effective interaction of these solvents with both the PANI chains (mainly through amine or imine nitrogens) and the counterions.

2) The solubility at room temperature of PANI-CSA$_{0.5}$ differs, not unexpectedly, from solvent to solvent, from around 1% w/w to more than 10% w/w.

3) Surprisingly, the conductivity of PANI films cast from these solutions is strongly dependent on the nature of the solvent. This value may be higher *or* lower than the conductivity of pressed pellets of the initially prepared PANI-CSA$_{0.5}$ powders. The data presented in Table 1, give the general impression that slightly acidic solvents (such as cresols) are more favorable for high values of the conductivity, while slightly basic solvents (*e.g.* NMP) usually yield PANI films of significantly lower conductivity; this is true despite the fact that the solubilities of PANI-CSA$_{0.5}$ in these two solvents are very close.

It is important to bear in mind that weakly acidic phenols (pKa = 10) and fluorinated alcohols are strong acceptors, while basic solvents such as NMP are strong donors. While both species are able to form strong secondary bonds to the polyaniline chains, these two types of solvent will effect the electronic state of conducting polyaniline chains in opposite directions. The acceptor power generally is quantitatively characterized by the acceptor number. The PANI salt solvents listed above may be ordered according to acceptor strength as follows:

$$NMP\ (13.3) < DMSO\ (19.3) < CHCl_3\ (23.1) < Phenols < R\text{-}COOH\ (52.9)$$
$$< H_2O\ (54.8) < R\text{-}SO_3H\ (126.1)$$
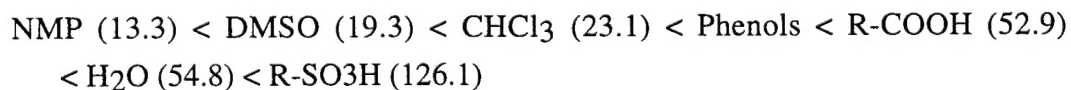
The acceptor properties of solvents interacting with a polyaniline chain may affect the electronic state of polyaniline in two different ways, each of which will produce an increase in the conductivity: first, it will increase the density of states of the polaron (*i.e.* charge carrier) band;

second, it will increase the density of positive charges on the PANI chain, which renders the macromolecule more rigid due to the increasing repulsion along its contour.

Acidity and donor/acceptor properties of the solvents are not the only factors which affect the electronic state of the polyaniline chains. For example, formic acid is more acidic and is a stronger acceptor than *m*-cresol. Many PANI salts are very soluble in formic acid; however, the conductivities of films obtained from formic acid solutions are significantly lower than those of materials obtained from *m*-cresol.

As a matter of fact, the data presented in Table 1 indicate that casting films from solvents with a high dielectric constant (for example NMP (ε = 32.0), DMSO (ε = 46.7) and formic acid (ε = 58.5), relative to that of *m*-cresol (ε = 1.8), yield PANI materials with very low conductivity. Clearly, solvents with higher dielectric constant can screen the Coulomb interactions between charges on the PANI chain and between the counterion and the positively charged PANI chains. These screening effects lead to a decrease of the PANI chain stiffness, as is evident from the decreasing viscosity of solutions in solvents of increasing dielectric constant.

The size of the solvating compounds may also be important. Steric hindrance effects due to bulky solvating agents bound to the PANI chains would increase the chain stiffness.

§3.1.2 PANI salts with other counterions
It is well established that the conductivity of a PANI salt is strongly dependent on the nature of the counterion. This is true both for conducting materials prepared by direct polymerization of aniline in aqueous solutions in the presence of a protonic acid, and for those prepared by protonation of emeraldine base films cast from solution. Many authors have reported that the critical determinant of the conductivity of polyaniline produced by a particular method is the strength of the acid used (pKa). However, our studies of the conductivity of PANI films cast from organic solvents indicate that the conductivity also significantly depends on the nature of the counterions. In addition, we observed that, depending on the particular combination of solvent and counterion, the conductivity of films cast from organic solvents may be either higher *or* lower than that of pressed pellets of the initial PANI salt powder.

In Table 2 we compare the electrical conductivities of pressed pellets of polyaniline salt powders protonated with different sulfonic acids counterions with that of films cast from solutions in *m*-cresol and DMSO Solubility data are also given.

Table 2.
Solubility in *m*-cresol and DMSO of PANI salts protonated with different protonic acids, and conductivities of pressed pellets and cast films.

R-sulfonic acid	Solubility (% w/w)		Conductivity (S/cm)		
			*Powder**	*Film* cast from	
R	*m*-cresol	DMSO		*m*-cresol	DMSO
(±) camphor-10-	4-10	4-8	10	200-400	3×10^{-2}
(+)-3-bromocamphor-10-	2-6		—	120	
(+)-bromocamphor-8-	2-6		—	100	
dodecylbenzene-	1	0	20	80-100	—
p-toluene-	0.5	d	20	50-100	—
p-chlorobenzene-	0.5	d	20	10^{-2}	—
trichlorobenzene-	0.5	3.2	10	10^{-6}	2×10^{-2}
4-nitrotoluene-2-	0.5	2.0	10^{-1}	10^{-5}	3×10^{-1}
m-nitrobenzene-	d	—	5	—	2
2-hydroxy-4-methoxy-benzophenone-5-	2	d	10^{-1}	10^{-1}	10^{-7}
4-hydroxybenzene-	?	1.5	6	?	3×10^{-2}
3-pyridine-	0	1.5	10^{-1}	—	2×10^{-5}

* 0.5 mole acid (per PhN unit) was mixed with PANI emeraldine base and pressed between hot plates at 165 ° for 1 min.

From the data collected in Table 2 we draw the following conclusions:

1) The solubility of PANI salts depends mainly on the compatibility of the solvent and the organic "tails" of the counterions. The common rule of miscibility, *i.e.* "polar in polar and non-polar in non-polar", is true for these complex systems. For example, PANI-DBSA$_{0.5}$ is completely insoluble in DMSO, and PANI-(*m*-nitrobenzenesulfonic acid)$_{0.5}$ is nearly insoluble in *m*-cresol.

2) The electrical conductivity of films cast from the same solvent varies over a very wide range for different counterions; this is true even in cases where the conductivity of pressed pellets (*i.e.* that of the material prior to dissolution) is nearly the same. For example, the conductivities of PANI-CSA$_{0.5}$ and PANI-(trichlorobenzenesulfonic acid)$_{0.5}$ cast from *m*-cresol differ by more than 8 decades, while the values for the initial

powders were comparable. This remarkable finding clearly indicates that the conformation of PANI-salts in solution is strongly dependent on the interactions between the PANI chains, counterions, and solvents. In the case of PANI films cast from solutions in the polar solvent DMSO, counterions with polar tails generally yield higher conductivities although they never exceed the values for the initial pressed pellets. This is consistent with the results in Table 1.

§3.1.3 Solution behavior of PANI-CSA$_{0.5}$ in mixed solvents

In order to gain a deeper understanding of the interactions of solvents with PANI salts, we conducted a study of the dissolution behavior of the model system PANI-CSA$_{0.5}$ in mixtures of solvents and compared the results with that in the corresponding pure solvents. The various PANI-CSA$_{0.5}$ solutions were prepared in three different ways:

Method A: PANI-CSA$_{0.5}$ powder was added to a mixture of *m*-cresol and a second solvent at room temperature. Three different ratios of *m*-cresol to the second solvent were used: 4:1; 1:1; or 1:4. This method was applied for all solvents investigated.

Method B: *m*-cresol was added to a solution of PANI-CSA$_{0.5}$ in a different solvent, referred to as the "second solvent". The ratio of *m*-cresol to the PANI-CSA$_{0.5}$ solution in the second solvent was 1:10; 1:5; or 1:2. This procedure was employed only for those second solvents in which PANI-CSA$_{0.5}$ can be dissolved.

Method C: A second liquid was added into a 2 % w/w PANI-CSA$_{0.5}$ solution in *m*-cresol. The ratio of the PANI-CSA$_{0.5}$ solution in *m*-cresol to the second solvent was 10:1; 5:1 or 2:1. Some non-solvents for PANI-CSA$_{0.5}$ were also used in combination with *m*-cresol.

Qualitative results of these experiments are summarized in Table 3.

Table 3.
Solubility behavior of PANI-CSA$_{0.5}$ in mixed solvents prepared by different routes, and conductivites of solids derived thereof.

Solvents	Method A		B		C	
	Solubility	σ, S/cm	Solubility	σ, S/cm	Solubility	σ, S/cm
m-cresol/DMSO	<*m*-cresol[†]	as DMSO	homogeneous	as DMSO	gel	~*m*-cresol
m-cresol/NMP	insoluble	N/A	homogeneous	as NMP	precipitation	N/A

m-cresol/benzylal-cohol	decreased	~benzylalcohol	homogeneous	as benzylalcohol	homogeneous	~m-cresol
m-cresol/HCOOH	unchanged	as m-cresol	homogeneous	as m-cresol	homogeneous	as m-cresol
m-cresol/CHCl$_3$	<m-cresol	~m-cresol*	homogeneous	between two	homogeneous	as m-cresol
m-cresol/chloro-benzene	as m-cresol	~m-cresol*		homogeneous	as m-cresol	
m-cresol/tri-chloro-benzene	as m-cresol	~m-cresol*			homogeneous	as m-cresol
DMSO/CHCl$_3$	as DMSO	as DMSO				
DMSO/chloro-benzene	as DMSO	as DMSO				

† homogeneous solution upon mixing obtained only in mixture where weight fraction of DMSO larger than m-cresol, otherwise completely insoluble.
* conductivity is decreasing with increasing second solvent.

From the information collected in this table we conclude that:

1a) Remarkably, when a very small amount (10 % w/w, based on m-cresol) of DMSO was added to the PANI-CSA$_{0.5}$/m-cresol solution (method C), a PANI-CSA gel immediately precipitated from solution. The value of the conductivity of the resulting gels was very close to that of films obtained by evaporation from cast m-cresol solutions. Clearly, although its solvent power is almost the same as that of m-cresol, DMSO is a poor solvent for PANI-CSA$_{0.5}$ salt solvated by m-cresol.

This interesting result is consistent with a previous observation that PANI-CSA$_{0.5}$ in m-cresol has a rigid conformation (based on the observation of lyotropic behavior of this system). It appears that the rod-like PANI-CSA macromolecular salt is solvated by m-cresol molecules, preventing penetration of DMSO through this layer, which would cause a rod to coil transition. Upon addition of DMSO to the polyaniline solution, the PANI-CSA$_{0.5}$ precipitated in its rod-like configuration, consistent with a previously observed gel-formation and the high conductivity in the solid state.

1b) By contrast to the above observations, when m-cresol was added into a solution of PANI-CSA$_{0.5}$ in DMSO, the solution remained homogeneous at all ratios of the two solvents. The fact that the conductivity of the films derived from these solutions is essentially identical to those cast from pure DMSO indicates that no significant interaction occurred between m-cresol and the dissolved PANI chains.

These two experiments clearly point to a very strong solvation of the PANI salt by both DMSO and m-cresol.

1c) PANI-CSA$_{0.5}$ is not soluble in mixtures of m-cresol and DMSO in which the weight fraction of DMSO is less than or equal to that of m-cresol [Method A]. This finding seems to indicate that m-cresol has a stronger affinity for PANI. This is easy to understand since the polyaniline chain is a strong donor, and the stronger acceptor (m-cresol) should have a greater affinity for PANI (*cf.* acceptor number, above).

1d) NMP behaves very similarly to DMSO. The only difference is that PANI-CSA$_{0.5}$ salt cannot be dissolved in mixtures of NMP and m-cresol in *any* ratio (method A). This finding indicates that NMP has a weaker interaction with PANI than DMSO. Again, this is consistent with the acceptor strength ranking listed above.

1e) Formic acid, which is also a bad solvent for PANI-CSA$_{0.5}$, behaves very differently from DMSO and NMP. First, no precipitation occurred using any method of dissolution or mixing (A, B or C). Second, the conductivity of films cast from formic acid/m-cresol mixtures (by standard evaporation) were invariably identical to that for films obtained from pure m-cresol. This behavior can be readily understood on the basis of conformational changes. Since formic acid is much more acidic than m-cresol, it will preferentially solvate the PANI chains, displacing m-cresol. This behavior is confirmed by solution spectra which display the typical absorption curves for PANI-formic acid solutions in the presence or absence of m-cresol. The high conductivity of films cast from formic acid/m-cresol mixtures is due to the much lower boiling point of formic acid, which evaporates first and leaves an essentially pure solution of PANI in m-cresol from which the polyaniline salt films subsequently are formed.

2) When substances were used that are non-solvents for PANI-CSA$_{0.5}$ but which are miscible in any ratio with m-cresol (*e.g.* chlorobenzene and 1,2,4-trichlorobenzene in method A and B), the solubility and film conductivity retained the values measured for pure m-cresol systems. Unlike in the case of formic acid, the boiling points of these species are close to or exceed that of m-cresol.

3) The pairing of CHCl$_3$ with m-cresol behaved more like a traditional mixture of a good and a bad solvent. Clearly, the interactions of CHCl$_3$ with PANI chains are weaker than those with m-cresol (but strong enough to dissolve PANI-CSA$_{0.5}$ at least slightly). In mixing methods A and C, we observed a gradual change both of the solubility and the conductivity, depending on the relative ratio of two solvents. It should be noted that this behavior is consistent with the position of CHCl$_3$ between m-cresol and DMSO in the acceptor ordering.

4) Similar results were obtained when DMSO was used (instead of *m*-cresol) in combination with the other solvents. Results for the systems DMSO/CHCl$_3$ and DMSO/chlorobenzene are presented in Table 4.

§3.2 Type II solvents for polyaniline salts

§3.2.1 PANI-DBSA$_{0.5}$ in non-polar solvents

MacDiarmid *et al.* at the University of Pennsylvania have reported that (metallic) polyaniline has a optimum degree of protonation of 0.5 (molar ratio H$^+$/PhN = 0.5), at which the conductivity reaches its maximum value. In earlier studies we attempted to dissolve polyaniline protonated with dodecylbenzenesulfonic acid (DBSA) in non-polar solvents such as xylene, toluene or decalin. In that work we observed that the PANI salt is soluble only when DBSA is present in a molar H$^+$/PhN ratio that exceeded 0.5 ("excess" DBSA $\geq$ 0.25 mole per PhN unit). Initially, it seemed that PANI-DBSA$_{0.5}$ in the absence of additional DBSA exhibits some slight solubility (1-2%) in toluene. However, determination of the actual molar ratio of DBSA to PANI repeat units in the resulting solution showed that this value is *ca.* 1.0 in the final solution, even if the initial DBSA/PhN ratio is only 0.5. *Clearly, the observed increase of the DBSA/PhN ratio in solution is due to a partial deprotonation of part of the PANI salt, which forms an insoluble solid in the solutions.* Similar results were obtained for other aprotic organic solvents like xylene, chlorobenzene, decalin, *etc.* Comparing the solubility and actual DBSA/PhN ratio in solution we can draw several important conclusions:

1) The ratio of DBSA to PhN units should be approximately equal to 1.0 in order to render PANI-DBSA complexes soluble in non-polar solvents like toluene, xylene, decalin, chlorobenzene, trichlorobenzene, *etc.*; *i.e.* about one counterion molecule is required *per* nitrogen atom of the PANI chain.

2) The phase comprising material with the molar ratio H$^+$/PhN = 1.0 is the more stable phase in solution, and is drawn into solution by shifting the equilibrium of the following reaction to the right hand side:

$$2 \text{ PANI-DBSA}_{0.5} \longleftrightarrow \text{PANI-DBSA}_{1.0} + \text{PANI-EB}$$

where EB denotes the non-protonated emeraldine base form of polyaniline.

3) Increase of the DBSA/PhN ratio beyond 1.0 does not markedly increase the solubility of PANI-DBSA. Nevertheless, we found that the stability of PANI-DBSA solutions against gelation increased with increasing DBSA/PhN ratio.

PANI-DBSA$_{1.0}$ films cast from solution are relatively soft and sticky, due to the presence of the excess DBSA. The latter can be easily removed by extraction with any of a number of organic

solvents, *e.g.* acetone. The conductivity of the resulting free-standing PANI-DBSA$_{0.5}$ films is found to be slightly higher than that before washing (presumably due to the increase of the film density). It is apparent that the additional amount of protonic acids acts as a co-solvent which is absolutely necessary for dissolution of polyaniline in aprotic organic solvents. The additional 0.5 moles of protonic acid molecules are associated with the remaining, non-protonated, nitrogen atoms of the PANI-(acid)$_{0.5}$ salts, acting to decrease interaction between PANI chains and increase interaction between PANI and appropriate solvents.

Comparing results for the two classes of solvents, we conclude that the dissolution mechanism is the same, the only difference being that in the case of Type I solvents the solvent itself plays the role of solvating agent/co-solvent.

§3.2.2 Neutral co-solvents for PANI-DBSA$_{0.5}$/non-polar solvent systems

From a practical point of view, the presence of an excess of acid (*i.e.* molar ratios H$^+$/PhN>0.5) is undesirable. This excess acid renders the resulting polyaniline film highly acidic, corrosive and hygroscopic. From the above results regarding the mechanism of dissolution of PANI salts, it is a natural extension to employ neutral (or less acidic) additives as co-solvents which have a structure consisting of a strong hydrogen bonding group on one side and an organic tail that is compatible with the solvents of choice on the other. In this work, a wide variety of such substances (including alkyl substituted phenols, esters, amides and salts of alkyl or alkylaryl carboxylic and sulfonic acids) were examined for their ability to induce solubility of PANI-DBSA$_{0.5}$ in the non-polar solvent xylene. Some selected results are listed in Table 4.

Table 4.

Solubility of PANI-DBSA$_{0.5}$ in xylene in the presence of neutral co-solvents

Compounds (C)	C/PhN* molar ratio	solubility** (% w/w)
2,6-dimethylphenol	1.0	1.9
4-(tert-octyl)phenol	1.0	4.4
4-dodecylphenol	0.5	5.0
3-pentadecylphenol	0.5	6.8

4-dodecylresorcinol	0.5	1.4
p-hydroxybenzoic acid n-amyl ester	0.5	3.7
p-hydroxybenzoic acid n-dodecyl ester	0.5	3.8
p-hydroxybenzoic acid benzyl ester	0.5	0.5
gallic acid dodecyl ester	0.25	0.9
gallic acid dodecyl ester	0.50	3.3
gallic acid stearyl ester	0.25	3.3
gallic acid dodecyl ester	0.10	1.8
p-toluenesulfonic acid /methyl ester	0.5	2.0
p-toluenesulfonic acid/ethyl ester	0.5	2.0
p-toluenesulfonic acid /n-hexyl ester	0.5	0.4
dodecylbenzenesulfonic acid/ethyl ester	0.5	0.6
stearic acid/3-hydroxyphenyl ester	1.0	1.0
stearic acid /3,5-dihydroxyphenyl ester	1.0	2.0
4-hydroxyphenyl hexanamide	1.0	0.5
dodecylbenzenesulfonic acid/Zn salt	0.5	4.2
dodecylbenzenesulfonic acid/Cu salt	0.5	4.6
dodecylbenzenesulfonic acid/ 3-hydroxydiphenylamine salt	0.5	5.0
dodecylbenzenesulfonic acid/ 3-aminophenol salt	0.5	4.8
dodecylbenzenesulfonic acid/ 4-aminophenol salt	0.5	0.9
dodecylbenzenesulfonic acid/ 2-aminophenol salt	0.5	0.8
dodecylbenzenesulfonic acid/Al salt	0.5	0.6
4-ethylbenzenesulfonic acid/Zn salt	0.5	0.5
tri-ethanoamine lauryl sulfate	0.5	0.3
di-ethanol amine lauryl sulfate	0.5	0.4

* molar ratio of additive to conducting PANI repeat unit (PhN).
** PANI-DBSA$_{0.5}$ complex in initial mixture was 8 % w/w.

Similar results were obtained for the solubility of PANI-DBSA$_{0.5}$ in toluene and chlorobenzene. For several selected neutral additives a more detailed study was conducted. The results of that work are summarized in Table 5.

Table 5.
Effect of molar ratio of neutral additive on the solubility and conductivity of PANI-DBSA$_{0.5}$

Additive (CS)	CS/PhN initial	molar ratio in solution	Solubility (% w/w)	Conductivity (S/cm)
pentadecyiphenol	0.25	0.47	5.1	17.5
	0.50	0.64	6.0	19.6
	1.00	1.20	6.2	25.6
p-hydroxybenzoic acid/				
n-amyl ester	0.25	0.66	4.7	13.6
	0.50	1.19	5.5	17.1
	1.00	1.89	5.2	12.6
dodecylresorcinol	0.25	1.15	2.4	10.8
	0.50	5.00	1.1	4.0
	1.00	7.00	1.8	1.0
3-aminophenol-dodecyl				
benzenesulfonic acid	0.25	0.49	4.8	30.3
	0.50	1.40	3.5	25.9
	1.00	2.30	3.3	24.6

Analysis of the data in Tables 4 and 5 leads to the following conclusions:

1) Among the factors affecting the solubilizing power, most important are the pKa of the co-solvents, the length of the alkyl groups, the solubility of the additives themselves in the organic solvent and the steric environment around the hydrogen bonding sites.

2) For optimal additives, 0.5 mole of additive *per* one Ph-DBSA$_{0.5}$ unit is sufficient to dissolve PANI-DBSA$_{0.5}$ complexes in reasonable concentrations. Further increase in the

amount of additive does not increase the solubility greatly. This behavior is similar to that of excess DBSA.

3) The conductivity of free-standing PANI films obtained by casting and washing films with acetone is slightly lower than that of those prepared with excess DBSA, but the values are very close.

Thus, we conclude that appropriately selected additives can be used to dissolve PANI-DBSA$_{0.5}$ in non-polar solvents, and that the films cast from such solutions exhibit properties that are comparable to those of films cast in the presence of an excess of DBSA.

§3.2.3 Neutral co-solvents for PANI-CSA$_{0.5}$/non-polar solvent systems

It is important to note that by carefully selecting co-solvents, polyaniline complexes protonated with acids that do not feature the long alkyl side groups of DBSA (such as toluenesulfonic acid (TSA) or the more polar camphorsulfonic acid (CSA)) can be dissolved in non-polar organic solvents such as toluene or xylene. Unlike DBSA, the acids CSA and TSA themselves are *not* soluble in these organic solvents. Table 6 shows the solubility data of PANI-CSA$_{0.5}$ in toluene and PANI-TSA$_{0.5}$ in chlorobenzene in the presence of neutral co-solvents.

Table 6.
Solubility of PANI-CSA$_{0.5}$ in toluene and PANI-TSA$_{0.5}$ in chlorobenzene in the presence of neutral co-solvents

Co-solvent (CS)	PANI-CSA$_{0.5}$			PANI-TSA$_{0.5}$		
	CS/PhN* ratio	solubility** (% w/w)	σ (S/cm)	CS/PhN* ratio	solubility** (% w/w)	σ (S/cm)
p-dodecylphenol	1.0	1.1	-	-	-	-
3-pentadecylphenol	0.5	0.6	-	1.0	2.3	16
4-dodecylresorcinol	0.5	5.0	12	1.0	0.5	3
p-hydroxybenzoic acid/dodecyl ester	0.5	2.0	1	1.0	0.0	_
p-hydroxybenzoic acid/n-amyl ester	0.5	0.1	-			
3-aminophenol-DBSA	0.5	3.0	2	1.0	3.3	0.3
DBSA	0.5	4.8	22	0.5	2.4	23

* molar ratio of additive to a conducting PANI repeat unit (PhN).
** PANI-CSA$_{0.5}$ and PANI-TSA$_{0.5}$ complex in starting mixture was 5 % (w/w).

The solubility of PANI-CSA$_{0.5}$ is strongly dependent on the chemical structure of the additive. Some co-solvents which are effective in dissolving PANI-DBSA$_{0.5}$ in non-polar solvents are completely inadequate for PANI-CSA$_{0.5}$. Surprisingly, PANI-TSA$_{0.5}$ exhibits a lower solubility in toluene than that PANI-CSA$_{0.5}$ in the presence of the same co-solvent. PANI-TSA$_{0.5}$, however, has a solubility in chlorobenzene comparable to that of PANI-CSA$_{0.5}$ in toluene.

As can be seen in Table 6, the solubility of PANI-CSA$_{0.5}$ in toluene is generally much lower than that of PANI-DBSA$_{0.5}$ in the presence of the same co-solvents (compare Table 5). However, dissolution of PANI-CSA$_{0.5}$ in non-polar organic solvents requires that the co-solvent solvates not only the polyaniline chain but also the polar CSA counterion.

It is obvious from the data in Table 7 that to dissolve PANI-CSA$_{0.5}$ in non-polar solvents such as toluene at least one mole of co-solvent per PhN-CSA$_{0.5}$ repeat unit is necessary (*i.e.* one molecule of co-solvent per every imine or amine nitrogen). This is to be contrasted with the case of PANI-DBSA$_{0.5}$ where only 0.5 mole of neutral co-solvent or excess DBSA molecule per nitrogen is necessary to dissolve the salt.

Table 7.
Comparison of co-solvent content in initial mixture and
in the resulting solution of PANI-CSA$_{0.5}$ in toluene.

Co-solvent (CS)	Initial CS/PhN ratio	CS/PhN ratio in solution
dodecylresorcinol	0.25	0.0
	0.50	1.1
	0.75	1.0
	1.00	1.1
	1.25	1.2
	1.50	1.5
dodecylbenzenesulfonic acid	0.50	1.0
	1.00	1.1

From these results we conclude that in the case of PANI-CSA$_{0.5}$ the additional 0.5 mole of co-solvent is required to solvate the CSA counterions and increase the interactions of the formed PANI complexes with toluene.

§3.2.4 Neutral co-solvents for PANI salts with highly polar counterions

We attempted to dissolve polyaniline protonated with acids containing highly polar organic groups (such as a nitro group) in the presence of the same co-solvents which were found to be good co-solvents for PANI-CSA and TSA salts. The results are summarized in Table 8. We found the all neutral phenols, resorcinol, and the esters listed in Table 6 were not effective for dissolution of these complexes in the any excess of additives with the exception of DBSA itself and a few DBSA salts (such as 3-aminophenol-DBSA salt in a 1:1 or more molar ratio to the PANI complex).

Table 8.
Comparison of the solubility of PANI protonated with different counterions in the presence of the same co-solvents.

R in R-SO$_3$H	Solubility (w/w%)		Conductivity (S/cm)		
	3-APh-DBSA*	DBSA	3-APh-DBSA	DBSA	powder
p-chlorobenzene-	0.6	3.9	0.5	30.0	20
trichlorobenzene-	1.5	0.7	0.7	7.0	10
m-nitrobenzene-	1.6	0.5	6.8	10.0	5.4
p-nitrotoluene-2-	0.8	0.7	56.1	5.1	0.1
p-hydroxybenzene-	0.2	0.3	5.5	25.0	6.3
3-pyridine-	1.0	0.8	0.4	19.2	0.1

*3-APh-DBSA = reaction product of 3-aminophenol and dodecylbenzene sulfonic acid.

Table 8 compares solubility of polyaniline protonated by different counterions with very polar organic groups in the presence of co-solvents. Solubility is generally low due to the highly polar nature of counterions.

Finally, we observed that the solubility of PANI-DBSA$_{0.5}$ is extremely sensitive to the presence of water in the system. For example, PANI-DBSA$_{0.5}$ salt prepared without special efforts to eliminate traces of absorbed moisture is *completely insoluble* in toluene or xylene. The effect of water decreases with increasing initial DBSA/PhN ratio. We attribute this to competition between the different solvating agents, *i.e.* between DBSA and H$_2$O. Hence, the effect of water on the solubility *and* on the conformation of the PANI chain should be dependent on the ratio of the acceptor powers of water and the co-solvents. For example, the solubility properties of PANI salts were found to be less sensitive to the water content in the case of *m*-cresol solution.

As indicated above, chloroform is a solvent of moderate acceptor strength. Its behavior is in between that of the Type I and II solvents for polyaniline. Fully-protonated PANI complexes can be only slightly dissolved in chloroform (up to *ca.* 1-2% w/w, depending on the counterion), much like the case for Type I solvents. On the other hand, we found that the concentration of PANI salt in solution increases markedly when the molar ratio of protonic acid to PANI units increases to unity. Table 9 shows the concentration of PANI-DBSA and PANI-CSA in chloroform, and the conductivity of films cast from these solutions.

Table 9.
Concentration of PANI-DBSA and PANI-CSA in chloroform
and conductivity of cast films from corresponding solutions.

PANI salt	Acid/PhN ratio		Solubility	Conductivity
	initial	in solution	(w/w %)	(S/cm)
PANI-DBSA	0.5	0.4	3.9	3
PANI-DBSA	1.0	1.1	4.2	19
PANI-CSA	0.5	0.49	1.8	3
PANI-CSA	1.0	1.03	4.2	10

A slight increase of the conductivity was found for films derived from solutions containing excess acid (molar ratio acid/PhN = 1.0). By contrast, for solutions of PANI salts in Type II solvents (such as NMP and DMSO), an increase in the protonic acid/PhN molar ratio did not

affect the conductivity. This observation again indicates the important influence of the solvating power on the conformation of polyaniline chains in solution and, consequently, on the properties of the solids processed from such solutions.

§4. Summary of Research on Solvent Processing of Conducting Polyaniline

From a detailed analysis of the behavior of two general types of organic solvents for conducting polyaniline, we conclude that fully protonated polyaniline (ratio $H^+/PhN = 0.5$) can be dissolved in a given organic solvent only in cases where the PANI-(acid)$_{0.5}$ complex is solvated by an appropriate solvating agent. At least 0.5 moles per PANI unit (PhN) of the solvating agent must be present (this amount is dependent on nature of counterion and solvent, for example for very polar counterion in non-polar solvent this value is 1.0). The solvating agent can be the solvent itself if it has strong hydrogen bonding moieties, an excess amount of protonic acid, or some neutral compound with strong hydrogen bonding moieties which is compatible with the solvent.

We have shown clearly that the solution properties (solubility, conformation, *etc.*) of conducting PANI prepared by counterion induced processibility are strongly dependent on the interactions between the polymer chain, the counterions, and the co-solvent. The solid state properties (conductivity, crystallinity, *etc.*) of a PANI film processed from such a solution are dependent on the choice of counterion, solvent, and co-solvent. The co-solvent can be removed after processing without altering the solid state properties of the resulting polyaniline films or fibers.

All experimental results on PANI solutions and the solid state properties of PANI films processed from those solutions can be explained within the framework of the traditional materials science of polymer solutions and polymer electrolytes. There is no need to develop new theories or invoke novel mechanisms such as "secondary doping".

§5. Development of Specific Materials Technology for Producing Three Particular Conductive Products.

§5.1: Conductive Coatings for Transparent Conductive Electrodes.

Because the mechanical properties of pure polyaniline films are quite poor, we expect to use polyaniline blends in most commercial applications requiring transparent electrodes. UNIAX has directed its recent efforts in this area towards the resolution of two problems in the fabrication of these types of PANI electrode materials.

§5.1.1: Investigation of solution blending of PANI with a variety of commercial polymers, with attention to the surface resistance and transparency of films fabricated from such solutions. Table 10 summarizes the results of these studies.

Table 10.
Summary of Solution Processing of Conducting Blends with Substituted Sulfonic Acids
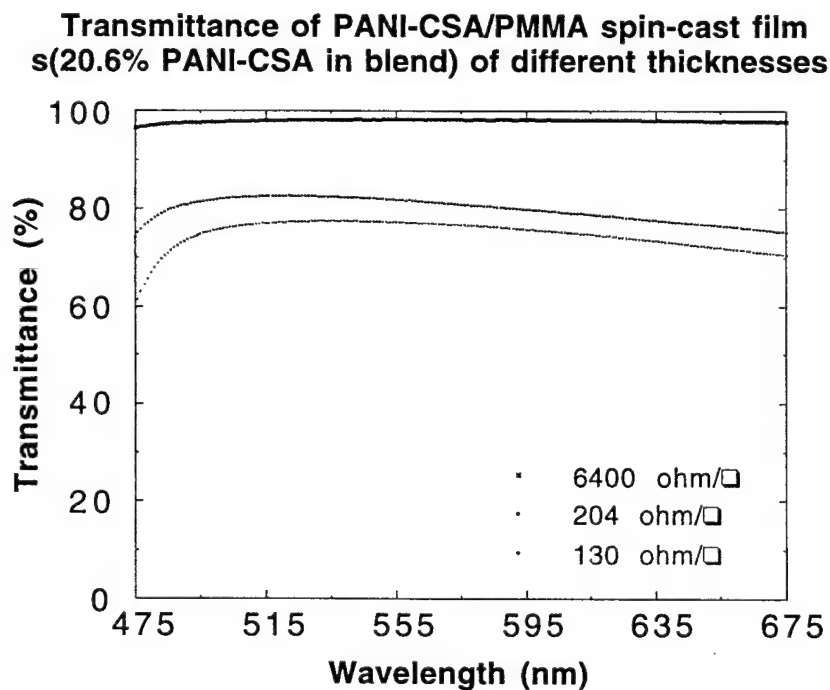
Host polymer	Acid	Solvent	Concentr. for $s=10^{-1}$S/cm	s_{max} (S/cm) at weight fraction	Remarks
Homopolymers:					
Polyethylene (PE)	DBSA	xylene, decalin	0.10 0.1 (0.30)	1-10 (0.30)	stretched unstretched
Polypropylene	DBSA	xylene	0.1	10 (0.40)	
Polystyrene (PS)	DBSA CSA	CHCl$_3$ m-cresol	0.20 0.01	1 (0.7)	transparent transparent
Polybutadiene	DBSA	xylene		3×10^{-6} (0.06)	
Polysiloxane	DBSA	xylene		1×10^{-6} (0.02)	
Nylon 46	CSA	m-cresol	0.07	10-50 (0.50)	homogeneous
Nylon 12	CSA	m-cresol	0.07	10-50 (0.50)	homogeneous
Zytel 330 (Du Pont, amorphous Nylon)	CSA	m-cresol	0.03		transparent
Polycarbonate (PC)	CSA	m-cresol	0.10	100 (0.60)	
Luran PC	CSA	m-cresol	0.02	32 (0.60)	transparent
Tetramethyl-bis-phenol PC	CSA	m-cresol	0.01		transparent
Polyacrylonitrile (PAN)	CSA	DMSO		10^{-3} (0.40)	transparent, no clear threshold
Polymethyl-methacrylate (PMMA)	CSA	m-cresol	0.01	70 (0.15-0.45)	transparent remarkable decrease
	DBSA	CHCl$_3$	0.10	10^{-1}(0.10)	less transparent than from m-cresol
Polyvinylacetate	CSA	m-cresol	0.03	50 (0.45)	transparent

Polyvinylbutyral	CSA	*m*-cresol	0.03	30 (0.30)	transparent
Polyvinyl-pyrrolidone	CSA	*m*-cresol	0.03		transparent
Polysulfone p-1700	CSA	*m*-cresol	0.02		
Polyester (Hars)	CSA	*m*-cresol	0.01		transparent
Copolymers:					
ABS	CSA	*m*-cresol	0.02	26 (0.40)	
Styrolux (polystyrene-butadiene)	CSA	*m*-cresol	0.03		transparent

§5.1.2: Optimization of the process parameters for fabrication of PANI blend films with good electrical conductivity and high optical transparency.

Because PANI absorbs optical radiation, the key issue in efforts to achieve a combination of high transparency with low surface resistance is reduction of the PANI loading necessary to reach a given level of conductivity. This is illustrated by the data in the figure immediately below. The

Transmittance of PANI-CSA/PMMA spin-cast films(20.6% PANI-CSA in blend) of different thicknesses

needed level of loading is dependent on the morphology of the conducting PANI component within the polyblends, which is, in turn, highly sensitive to the conditions of fabrication of the polyblend films. The figures below indicate two of the factors which we have investigated to det-

Effect of drying temperature on conductivity of PANI-CSA/PMMA blend
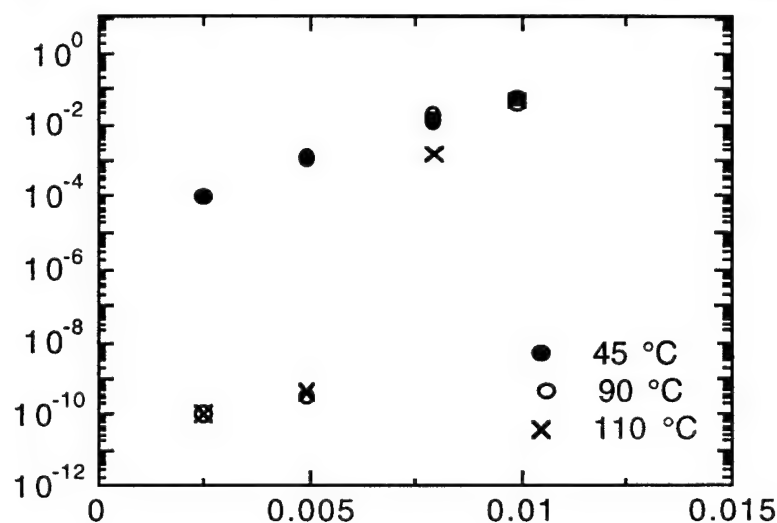
ermine their influence on the conductivity of the blends as a function of PANI loading. The data in the first figure (above) show that the conductivity of PANI-CSA/PMMA films depends on the temperature at which the excess solvent is driven off, following casting of the film:

Conductivity of PANI-CSA/PMMA blend films with PMMA of different viscosities (drying temperature: 50°C)
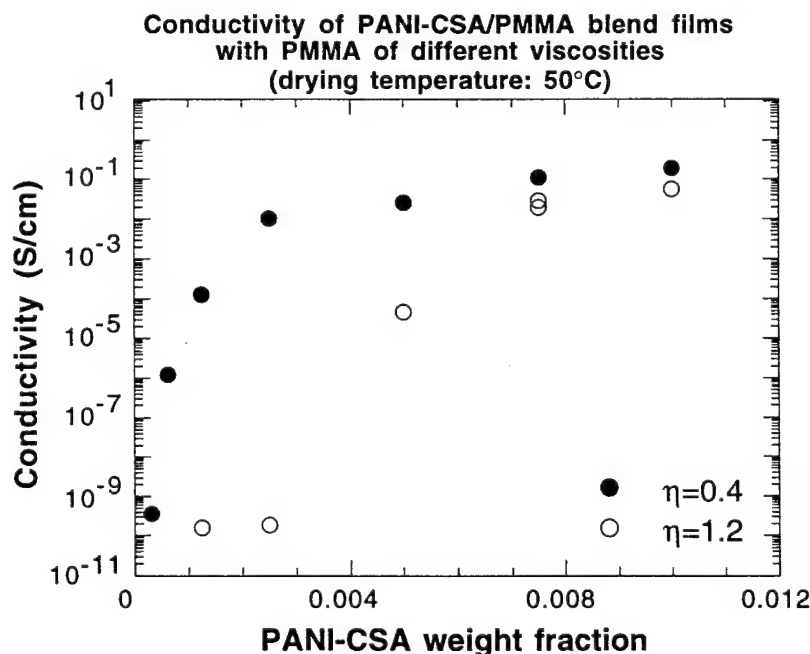
The data in the second figure (above) demonstrate that the conductivity of PANI-CSA/PMMA film can also be altered by preparing them from PMMA of different molecular weight.

The origin of these effects is explained by the microstructure of the PANI within the polyblends. Transmission electron micrographs show that under optimized preparation conditions an interpenetrating network of PANI fibrils forms within the inert host polymer. Using low molecular weight PMMA, a conducting PANI network forms at loadings as low as 0.5%(w/w).

§5.2: Conductive Paints.

We have performed some preliminary studies related to the use of polyaniline in conductive paints. These studies have been of two types:

1. Coating of insulating filler particles (TiO_2 or SnO_2) with PANI solution to form conducting filler particles;

2. Blending of commercial polymers, fillers and dyes with PANI complexes from solution to form paints.

Some of the results of these studies are summarized in Table 11 and the figures on the following page:

Table 11.
Conductivity of PANI-coated SiO_2 and TiO_2.

filler type	PANI salt	Solvent	Conductivity (S/cm)	weight fraction of PANI in filler(%w/w)*
SiO_2(EXP1-C)	PANI-DBSA	xylene	1.8×10^{-3}	2.3
SiO_2(EXP1-C)	PANI-DBSA	decalin	9.7×10^{-4}	
SiO_2(EXP1-C)	PANI-CSA	m-cresol	6.9×10^{-2}	

The figure below shows the Conductivity of SiO_2 coated with PANI from solutions of different PANI concentration:

Conductivity of PANI coated SiO_2 in diferent initial ratio of PANi to SiO_2
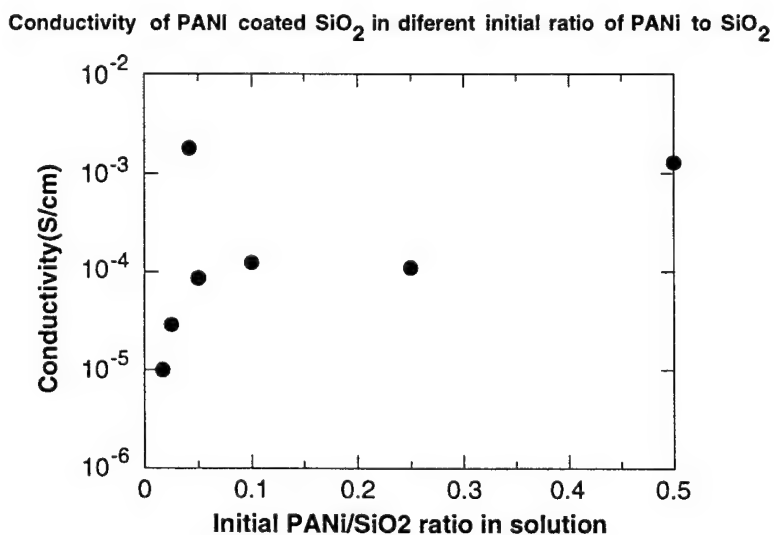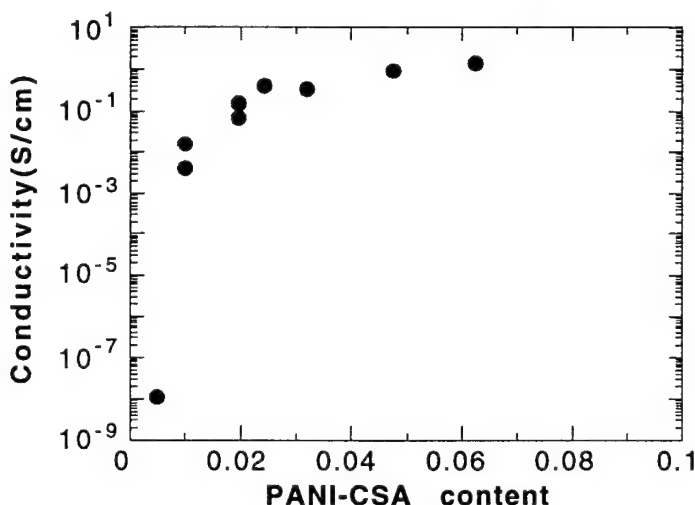
Several preliminary conclusions have been drawn from these data:

    a. Incorporation of pre-coated TiO_2 particles does not effect the conductivity of PANI/Nylon blends.

    b. A similar technique can be used to pre-coat particles of materials that will improve the mechanical properties of the resulting paint, as well as the dispersion of dyes or other supporting components in the paint.

    c. This technique can also be used to produce coated particles for use as conducting fillers in rubbers or engineering plastics.

Of relevance to the second type of experiment related to the formulation of conducting paints, some blends of PANI-CSA with Nylon 4,6 filled with TiO_2 particles were made and examined. The data in the figure below present the results of conductivity measurements of PANI-CSA/resin/TiO_2 blends for various PANI loadings in a composite containing 33% TiO_2.

**Conductivity of cast film of PANI-CSA in TiO_2(33%)/resin blend**

Here, one can draw the preliminary conclusion that the conductivity is influenced by several factors: the surface character of particles to be coated; identity of the counter-ions used as PANI dopants; solvent; and solution concentration. Optimization of these conditions will be the focus of work in the next stage of project.

§5.3: Conductive Epoxies

A recent investigation at UNIAX yielded thermally cured epoxy adhesives containing doped PANI with electrical conductivity suitable for antistatic applications. Bulk conductivities from 10^{-8} to 10^{-3} S/cm were demonstrated. The relevant conductivity data are summarized in the

figure below. By nature conventional Bisphenol A-type epoxy resins, aliphatic and cycloaliphatic epoxides, and doped polyaniline are dissimilar materials, which prevents their intimate mixing or
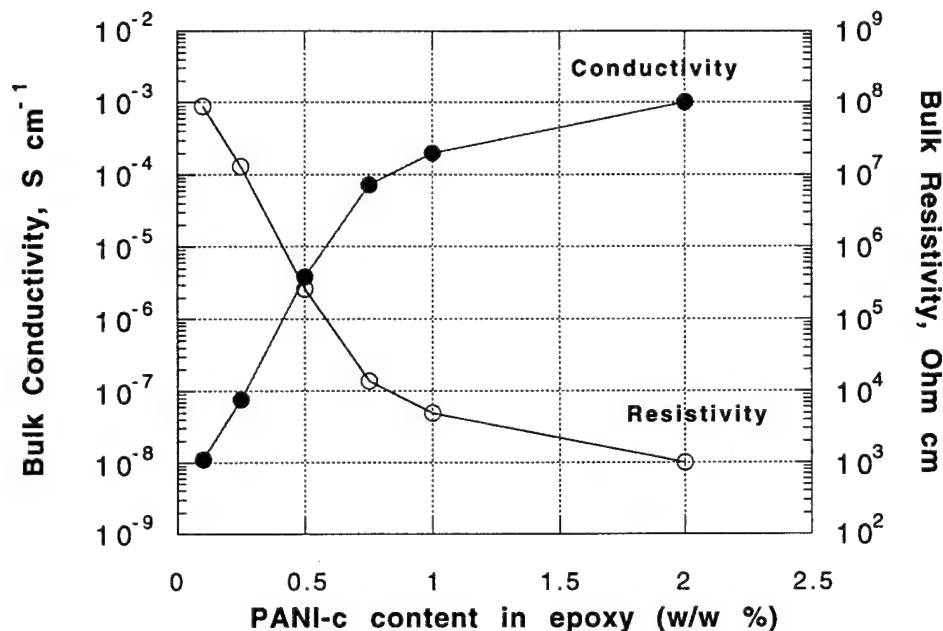
homogenization. A broad search, did, however, yield a low molecular weight, epoxy-compatible unsaturated compound (*or unsaturated alkylated phenolic resin*) in which doped PANI is soluble. Upon crosslinking, this compound co-reacted with the epoxy matrix, producing a 100% solid system without volatiles. In addition, it was found that the doped PANI solution was compatible with a variety of epoxy resins, indicating a possible route to coatings for a broad range of applications, with considerable formulation latitude. A paper entitled *"Preparation and Properties of Electrically Conducting Epoxy Adhesives With an Inherently Conducting Polymer"*, summarizing many of the principal results of this work is in preparation.

§5.3.1: Epoxy Preparation.

Emeraldine base, *i.e.* polyaniline in its non-conducting form, of intrinsic viscosity 1.2 dl/g, (measured at room temperature in 97% H_2SO_4) 0.1 w/w%, was mixed with (+/-) camphorsulfonic acid in a molar ratio of 1.0 to polymer repeat unit PhN in reagent alcohol for 2 hrs @ 50 °C. The alcohol was evaporated and the complex dried in a vacuum oven for 48 hrs. This polyaniline complex, now designated as **PANI-c**, exhibited a bulk conductivity of 2.0 S/cm as a pressed pellet (four probe method).

The **PANI-c** complex (0.5 gr.), was placed into 9.5 gr. of a **alkylated phenolic resin** and treated in an ultrasonic bath. The resulting mixture was a dark green solution of viscosity 500 cps, designated as **PANI/phenol blend**

The epoxy resin (weight per epoxide = 169) was mixed with the **Pani/phenol blend** under moderate heat, to provide green translucent solutions containing from 0 to 2.0 w/w % of **PANI-c** in a cured epoxy system employing Lewis Acid as a catalyst. Test coupons for bulk conductivity measurements as well as Thermogravimetric Analysis were prepared with cast thin films cured at 65 °C for 60 minutes in a forced air circulating oven.

§5.3.2: Epoxy Characterization.

Four epoxy formulations containing 0, 0.2, 0.5 and 1.0 w/w%, respectively, of **PANI-c,** (designated as Blends A, B, C and D) were selected for characterization and were evaluated for the properties summarized below:

VISCOSITY & POT-LIFE were measured with a Brookfield Cone & Plate Viscometer (Model RVDVII+CP) at 25 °C. In this study, pot-life was defined as the time required to double the initial viscosity of the blends containing the catalyst at 25 °C.

GEL TIMES for our formulations were estimated by measuring the time required for a given formulation to gel at 65 °C utilizing a Hot-Plate & Stirrer.

GLASS TRANSITION TEMPERATURES for the cured epoxy compositions were measured with a Differential Scanning Calorimeter (DSC, Mettler Instruments) employing 40 °C/min heating rates.

LAB SHEAR STRENGTH, based on the ASTM D-1002 guidelines, was tested employing acid etched aluminum test coupons. A loading speed of 0.05 in/min was employed with an Instron Tensile Tester.

TENSILE PROPERTIES, based on the ASTM D-638 guidelines, were evaluated with the Instron Tensile Tester. Test bars were made using a prefabricated Teflon mold into which the premixed and de-aired epoxy compositions were poured and cured as specified. Tensile strength at break, modulus of elasticity and ultimate elongation were evaluated at a 0.05 in/min test speed.

BULK CONDUCTIVITIES were measured using thin rectangular bars cut from the cured casts, to which tiny metal wires were attached with conducting paint (two probe method). Bulk resistances were measured with a Hewlett-Packard 4339A High Resistance Meter.

MORPHOLOGY of the cured epoxy films was evaluated with a Nikon Microphot FXA microscope at 100x magnification.

As is clear from the discussion above, the concentration of PANI-c in an epoxy matrix required for adequate dissipation has been demonstrated to be as low as 0.5 w/w%. This may be compared with the 10, 20 or even 30 w/w% used with typical conducting fillers such as carbon black, graphite fiber or various metal powders and flakes. A much lower percolation threshold of the sort commonly experienced with conventional inorganic fillers is observed with PANI-c, as indicated in the data in the following figure:
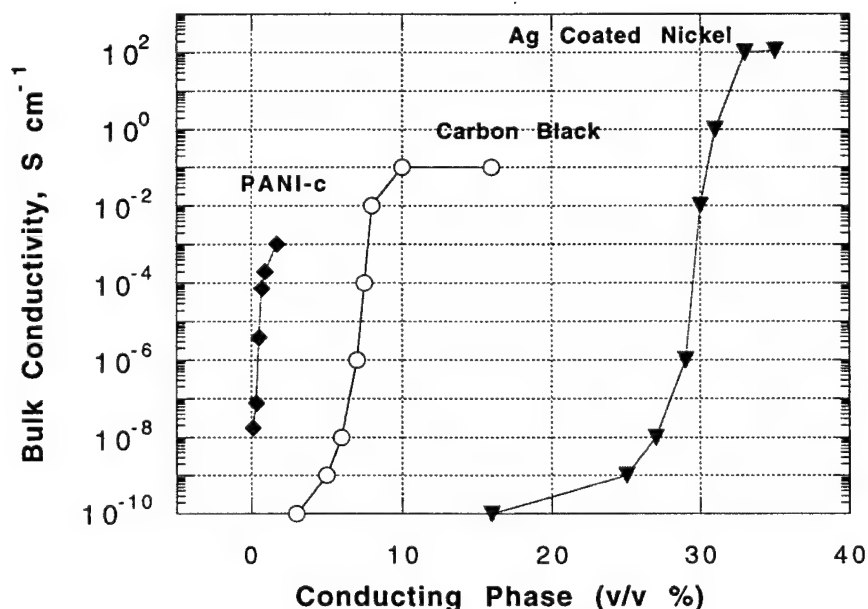
The PANI-c Technology has been found to be compatible with conventional epoxy resins such as Diglycidyl Ether of Bisphenol A, Phenol Novolak, cycloaliphatic resins and a variety of mono- and di-fuctional epoxy diluents. The Epoxy/PANI-c complexes react readily with acidic curing agents such as BF_3, BCl_3 complexes and their derivatives. Aliphatic amines are not

recommended. The suitability of other types of curatives with the PANI-c has not been fully investigated.

Table 12.
Effect of PANI-c Concentration on Properties of Epoxy Resin System

PROPERTIES, UNCURED[1]	Blend A	Blend B	Blend C	Blend D
Composition	2-Part	2-Part	2-Part	2-Part
Color	Tan	Green	Green	Green
Mix Viscosity @ 25 °C, cps	1,480	1,460	1,450	1,330
Pot-life @ 25 °C, mins	10	15	25	40
PROPERTIES, CURED[2]				
PANI-c, Weight %	0	0.2	0.5	1.0
Gel Time @ 65 °C, sec	20	30	40	70
Glass Transition, °C	80	68	50	46
Tensile Strength, psi	8,360	8,380	7,520	4,170
Modulus of Elasticity	247,390	249,990	219,850	117,570
% Elongation at Break	3.6	3.2	3.4	3.9
Lap Shear (Al/Al), psi	2,410	1,820	2,580	2,560
PROPERTIES, ELECTRICAL				
Bulk Conductivity, S cm^{-1}	1.0×10^{-15}*	1.0×10^{-8}	3.0×10^{-6}	2.0×10^{-4}

1. All systems were translucent, low viscosity liquids containing no solvents.

2. Mix ratio of 100 : 10 (epoxy : catalyst) by weight was maintained by all the compositions. Cure Schedule of 65 °C/60 mins was generally employed except for tensile bars which were first gelled at RT for 2 hrs followed by 2 hrs at 40 °C and finally cured at 65 °C for 2 hrs.

* Bulk conductivity of the control epoxy was not measured but instead a typical value was cited based on supplier technical literature.

§6. Related Research.

Through its codevelopment program with Neste Chemicals of Finland, UNIAX is also involved in the development of thermoplastic polyblends for, among other application, ESD and EMI shielding applications. Insights gained from this research and development effort also have an impact on the proposed Phase II research program. Although the problems associated with melt-processing and solution processing are distinct, the scientific issues which must be addressed are similar enough to allow for an important synergy between the two programs. In each case the project goal is to achieve compatibility between a supporting medium and the conducting form of PANI. The key strategy in both cases involves the use of functionalized dopant molecules

(surfactant counter-ions) to create this compatibility. Studies of the two routes provide information and "know-how" which enhance our understanding of the blending process and promote the success of both projects.

This is particularly clear in the case of recent discoveries (patent pending) made at UNIAX in which particular substituted aromatic compounds act as high temperature solvents for electrically conductive polyaniline. Analysis of the prior art of conducting polymer processing do not suggested any specific advantages of employing substituted aromatic compounds to render conductive polyaniline fluid during processing. It has been discovered at UNIAX that particular geometric arrangements of the various substituents in certain aromatic compounds are unexpectedly useful in dissolving protonated polyaniline. Additionally, some compounds may lead to the extremely unusual formation of useful crystalline solvates of electrically conductive polyaniline salt complexes and the particular substituted aromatic compounds. The latter compositions are remarkable in that they exhibit novel crystal structures that are different from either of their constituents; and have controllable melting temperatures.

Most of the representatives of this newly discovered class of compounds have high melting points in their neat form. When molten, these compounds readily dissolve protonated (conductive) polyaniline and form homogeneous compositions which:

i.   Do not contain excess protonic acid to render PANI processable;

ii. Display outstanding processability in the *fluid* form;

iii. Are substantially less acidic and less hygroscopic than previously studied materials ;

iv. Sometimes yield unusual crystalline structure.

EXAMPLE 1

An amount of $PANI(DBSA)_{0.5}$ salt (0.01 M), prepared according standard techniques, was mixed with 0.005 M stearyl gallate (SG) (Tokyo Kasei) in a miniature conical twin-screw extruder at 170 °C during 5 min. The resulting $PANI(DBSA)_{0.5}(SG)_{0.5}$ complex was pulled out from the orifice of the extruder as continuous filament. In the same manner, $PANI(CSA)_{0.5}$, $PANI(TSA)_{0.5}$ were complexed with SG at the same molar ratio at 170 °C for 5 min.

EXAMPLE 2

Example 1 was repeated, but ethyl gallate (EG) and phenylhydroxyquinone (PhHQ) were used at molar ratio 0.5 to $PANI(DBSA)_{0.5}$ instead of SG.

CHARACTERIZATION

The polyaniline compositions of Examples 1 and 2 were characterized by differential scanning calorimetry, conductivity of pressed pellets or films; and wide-angle X-ray diffraction patterns. Conductivity of thin films or pellets pressed at 170 °C measured by the usual four probe method are listed below in Table 12:

Table 13.
Conductivity of various conductive PANI salt complexes.

Composition	Conductivity (S/cm)
PANI(DBSA)$_{0.5}$	0.6
PANI(DBSA)$_{0.5}$(EG)$_{0.5}$	14.1
PANI(DBSA)$_{0.5}$(SG)$_{0.5}$	14.5
PANI(DBSA)$_{0.5}$(PhHQ)$_{0.5}$	2.2
PANI(CSA)$_{0.5}$	0.7
PANI(CSA)$_{0.5}$(EG)$_{0.5}$	7.0
PANI(CSA)$_{0.5}$(SG)$_{0.5}$	15.7
PANI(TSA)$_{0.5}$	-
PANI(TSA)$_{0.5}$(EG)$_{0.5}$	3.0
PANI(TSA)$_{0.5}$(SG)$_{0.5}$	10.3

The data in this table demonstrate that the conductivity values of the compositions with EG and SG additives is higher than in those without, despite the fact that the weight fraction of these [not electrically conductive] additives in the final compositions is ca. 30% and 50% for EG and SG, respectively.Melting points of these complexes were determined by differential scanning calorimetry (Mettler TA 3000; scan rate 10 °C/min), and are listed in Table 14 below.

Table 14.
Melting points of various PANI salt complexes.

Composition	Melting point (°C)
EG (for reference)	145.6
SG (for reference)	106.2

PANI(DBSA)$_{0.5}$(EG)$_{0.5}$	97.5
PANI(DBSA)$_{0.5}$(SG)$_{0.5}$	80.5
PANI(CSA)$_{0.5}$(EG)$_{0.5}$	130.2
PANI(CSA)$_{0.5}$(SG)$_{0.5}$	76.5
PANI(TSA)$_{0.5}$(EG)$_{0.5}$	111.2
PANI(TSA)$_{0.5}$(SG)$_{0.5}$	85.8

In the polarizing optical microscope, at the temperature denoted above, these complexes become transparent green highly viscous fluids, which displayed birefringence after mild shearing. These results indicate that the polyaniline complexes PANI(DBSA)$_{0.5}$, PANI(CSA)$_{0.5}$ and PANI(TSA)$_{0.5}$ [which themselves are not meltable below their respective decomposition temperatures] displayed a melting point after complexing with 0.5 mole (per one PhN unit) of these substituted aromatic compounds. The data also reveal that the melting temperature can be controlled by the selection of the chemical nature of these compounds.

Wide-angle X-ray diffraction patterns of (a) PANI(DBSA)$_{0.5}$, (b) SG and (c) the composition PANI(DBSA)$_{0.5}$(SG)$_{0.5}$ were recorded. From these patterns it becomes clear that a new crystal phase was obtained after complexing of PANI salts containing 0.5 moles protonic acid with the solvating compounds SG. All strong reflections of SG disappear after complexing and the spacings of PANI(DBSA)$_{0.5}$(SG)$_{0.5}$ are found at different angles from those of the initial PANI(DBSA)$_{0.5}$ complexes. In addition, it was revealed by these patterns that the crystallinity is also improved by the 0.5 mole solvating compound that were incorporated into PANI lattice. Similar results were obtained for the PANI(CSA)$_{0.5}$(SG)$_{0.5}$ and PANI(TSA)$_{0.5}$(SG)$_{0.5}$; and other substituted aromatic compounds such as EG, PG, DG and phenylhydroxyquinone.

These last results suggest unambiguously that conductive PANI salts may form crystalline solvates with substituted aromatic compounds of new crystal structures, and controlled melting temperatures.

§7. Status of Commercialization Activities.

Counter ion induced processing of the conductive polymer polyaniline, discovered shortly after the founding of the company in 1990, is now at an advanced stage of development. This important enabling technology created two different commercial opportunities:

- Formulation of thermoplastic polyblends incorporating conductive polyaniline for the manufacture of plastic parts with electrostatic dissipative or electromagnetic interference shielding properties;

- Formulation of a number of solvent-based products containing conductive polyaniline (*e.g.* coatings, paints, inks, epoxies, *etc.*) with analogous electrical properties for related applications.

UNIAX moved aggressively to establish a strategic alliance with Neste Oy, a major chemical manufacturer ($13 billion 1993 sales) based in Finland, to commercialize the first of these two applications. Together, the two companies are now completing work on scaling up production of large quantities of melt processible polyblends containing polyaniline, with initial product sales expected within two years. UNIAX will benefit primarily through the licensing of its proprietary technology which forms the basis of the commercialization alliance.

The second of the polyaniline-based technologies, conductive solution-based products, has been substantially developed with the support of the Air Force Office of Scientific Research through this contract, N° F49620-93-C-0011, a Phase II SBIR grant sponsored by the Ballistic Missile Defense Organization. Since the effective start date of this contract in February 1993, UNIAX has been actively seeking large industrial partners in the United States to aid in the commercial development of solvent-based products containing conductive polyaniline. A number of companies, including Monsanto, 3M, Dupont, and Allied-Signal, examined the technology and elected not to pursue it. UNIAX has subsequently moved to also license this technology to Neste Oy, the Finnish partner undertaking commercialization of the melt-processing technology. Their decision to license the solvent-processing technology was based, in part, on the desire of a number of U.S. manufacturers (predominantly in the automotive industry) to incorporate such materials in new value added products. UNIAX has retained the rights to use this technology in the development and planned production of light emitting devices based on electroluminescent polymers. These latter activities have become the central business focus of UNIAX Corporation.